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TITLE: **PROCESS TO SEQUESTER CO_2 IN NATURAL GAS HYDRATE FIELDS AND SIMULTANEOUSLY RECOVER METHANE**

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CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending U.S. patent application Serial No. 10/728,332, filed 04 December 2003.

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PROCESS TO SEQUESTER CO_2 IN NATURAL GAS HYDRATE FIELDS AND SIMULTANEOUSLY RECOVER METHANE

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to a process for storage and sequestration of carbon dioxide (CO_2). More particularly, this invention relates to a process for underground storage and sequestration of carbon dioxide in submerged sea areas of natural gas hydrate deposits.

Description of Related Art

[0002] Levels of anthroprogenic greenhouse gases, including carbon dioxide, in the Earth's atmosphere have been increasing substantially over the years due primarily to the burning of fossil fuels to supply about 80 percent of the world's energy needs. These increased emissions of greenhouse gases are believed responsible for a one degree Fahrenheit increase in the global average temperature over the past several years and if nothing is done to reduce them, the Earth will continue to warm, resulting in a host of environmentally damaging consequences, according to some scientists. There exists a range of options available for addressing this issue including the capture and storage of carbon dioxide produced in the combustion of fossil fuels. This involves three basic stages: capture, transportation and injection into a storage medium. Carbon dioxide capture would be most efficiently applied to large "point sources" in order to gain economies of scale both in the capture process itself and in subsequent transportation and storage. Examples

of such sources include fossil-fuel power stations, oil refineries, petrochemical plant, cement works and iron and steel plants. Because of the large quantities of gas involved (i.e. on the order of 1 - 30 Mt/yr CO_2 for a full scale scheme) transportation is most likely to be by pipeline in preference to batch handling, although liquefied gas tankers have been suggested as an option for a demonstration project. A range of storage options have been proposed, including injection into depleted oil and/or gas reservoirs, geological aquifers, deep unminable coal seams and on or below the deep ocean bed. Injection into oil/gas reservoirs and deep coal seams has the attraction of utilizing geological formations with demonstrated storage capabilities.

[0003] It is also known that the oceans naturally absorb carbon dioxide based upon which it is believed that one cost-effective way to mitigate global warming is to store the excess carbon dioxide in a liquid form in the depths of the ocean. Experiments to test theoretical predictions about the behavior of liquid carbon dioxide in the depths of the ocean have been conducted and the results indicate that under cool temperatures and high pressures, carbon dioxide and other greenhouse gases react with water to form a solid ice-like compound called clathrate hydrate. At shallow depths, liquid carbon dioxide will rise to the surface. But laboratory experiments with carbon dioxide hydrates suggest that liquid carbon dioxide put deep in the ocean would form a stable layer on the sea floor with a skin of solid hydrate as a boundary, like a pond covered by ice in winter. It is believed, however, that such a method has not yet been successfully demonstrated. Accordingly, there remains a considerable

interest in storage and sequestration of CO_2 on the bottom of the sea.

SUMMARY OF THE INVENTION

[0004] Accordingly, it is one object of this invention to provide a method for sequestration and storage of carbon dioxide.

[0005] It is another object of this invention to provide a method for sequestration and storage of carbon dioxide underwater.

[0006] It is still a further object of this invention to provide a method for sequestration and storage of carbon dioxide underwater with simultaneous recovery of methane gas.

[0007] These and other objects of this invention are addressed by a method for sequestration and storage of carbon dioxide in which the carbon dioxide to be sequestered and stored is injected into natural gas hydrate deposits disposed in terrestrial subsurface areas in order to displace the naturally occurring methane hydrates present therein with CO_2 hydrates. In this manner, the methane is produced by using the heat released from the CO_2 gas hydrate formation to drive dissociation of methane hydrate sediments. The recovered methane could be used to pay for the transportation and injection costs of CO_2 to the underwater site. Suitable fields of natural gas hydrate deposits are known to exist, for example, on sea bottoms in the Gulf of Mexico and Alaska.

[0008] In the parent application to this application, a process is disclosed in which a gas mixture comprising carbon dioxide and methane is brought into contact

with a methane hydrate solid material disposed in a reactor vessel, whereby the methane hydrate is displaced by carbon dioxide hydrate, thereby freeing the methane, which is then removed from the reactor vessel. Without wishing to be bound by any single explanation as to the operation of this invention, it is believed that the previously disclosed method for displacement of methane hydrate by carbon dioxide hydrate is the principle behind the operation of the invention disclosed and claimed herein.

[0009] Although described herein primarily in the context of natural gas or methane hydrates, it is to be understood that the method of this invention could be applied to any underwater or underground hydrate deposits where the hydrates in the deposit are less stable than CO_2 hydrates, and all such hydrate deposits should be considered to be within the scope of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

[0011] Fig. 1 is a schematic diagram showing a laser imaging system employed for the purpose of verifying the concept of this invention;

[0012] Fig. 2 is a graphical representation showing conditions for methane hydrate formation as part of the conceptual verification;

[0013] Fig. 3 is a laser image showing methane hydrate embedded in sediment;

[0014] Fig. 4 is a laser image showing methane hydrate embedded in the sediment near the sediment surface;

[0015] Fig. 5 is a laser image of the sediment after completion of a test to verify operability of this invention;

[0016] Fig. 6 is a diagram showing the gas chromatographic analysis of a gas phase sample (100 mole % CO_2) at the start of a test to verify operability of this invention; and

[0017] Fig. 7 is a diagram showing the gas chromatographic analysis of a gas phase sample after 68 hours (27.67 mol % of methane) of operation of a test to verify operability of this invention.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

[0018] The invention claimed herein is a method for sequestration and storage of CO_2 in which the CO_2 to be sequestered and stored is injected into a subterranean methane hydrate field whereby the methane in the methane hydrate field is displaced by the CO_2 and, in so doing, the methane is released for collection.

[0019] Both CO_2 and methane form structure I hydrates. At temperatures below about 283°K, there is a pressure range in which methane hydrate is unstable and CO_2 hydrate is stable. The heat released from the formation of CO_2 gas hydrate is larger than that needed for methane hydrate dissociation:

$$CH_4(H_2O)_n \rightarrow CH_4 + nH_2O \qquad \Delta h_f = 54.49 \text{ KJ/mole}$$

$$CO_2(H_2O)_n \rightarrow CO_2 + nH_2O \qquad \Delta h_f = 57.98 \text{ KJ/mole}$$

where n is the hydration number for methane hydrate and CO_2 hydrate (assuming that n is 6.15 for both methane and CO_2). It should be noted that n is dependent on pressure, temperature and the composition of the gas in the gas phase. This suggests that under certain pressure-temperature conditions, the replacement of CH_4 in the hydrate with CO_2 is thermodynamically possible.

[0020] To validate the concept of this invention, a laser imaging tool, shown in schematic diagram form in Fig. 1, was developed. The laser imaging tool comprises two primary components, a laser operation component 10 and an analytical component 11. As shown in Fig. 1, the laser operation component 10 comprises an air-cooled, solid-state diode laser 13 operating with a peak power of 200W at a wavelength of 808nm with pulse energy up to 20mJ, available from Oxford Lasers Company, U.K., a high-pressure sapphire cell 12 into which a sample to be tested is introduced, a diffuser 14 intermediate laser 13, and a high-resolution digital camera 21 capable of image capture at up to 10,000 frames per second disposed on a side of sapphire cell 12 opposite laser 13. The analytical component 11 comprises a high resolution digital camera control unit 19 operably connected to camera 21 and laser control unit 16 operably connected to laser 13. Also included within the analytical component 11 are a PC monitor 17 operably connected to a computer processing unit (CPU) 18 to monitor and store data, a video monitor 20 operably connected to the high resolution digital camera control unit 19 and a video cassette recorder 22 to record the imaging events in the sapphire cell 12. The laser imaging system is capable

of operating at high pressures (1500 psia) and low temperatures (- 40°C to 100°C).

[0021] To simulate undersea hydrate bed conditions and verify the concept of this invention, the high-pressure sapphire cell was packed with wet (water) sand sediment of about 30% porosity, similar to that of the Gulf of Mexico sediment, connected into the laser imaging system and charged with pure methane to a pressure of 700 psia. A NESLAB chiller, available from Thermo NESLAB, Portsmouth, NH, was used to cool and heat the cell at programmed rates (0.1°C per minute). The temperature of the cell initially was reduced from about 25°C to about 2°C. The pressure and temperature in the sapphire cell were measured simultaneously using a digital pressure sensor and thermocouple, respectively. Laser pulses from the laser illuminated the sapphire cell. The laser beam acts as a very short-duration strobe lamp for the high-speed digital camera, freezing the rapid action of hydrate formation and dissociation in the sediments in the sapphire cell. The high-resolution digital camera recorded the imaging events. A computer controlled the system while also collecting and processing pressure, temperature, time, and image data. Temperature and pressure measurements were tracked in real time.

[0022] Graphical software was used to update and display traces of temperature and pressure vs. time, and pressure vs. temperature. The hydrate formation process was monitored in real time. Images were captured during the heating and cooling cycle at a rate of 40 frames per second using a high-resolution and high-speed digital camera and processed using VISILOG software, available from NorPix, Inc.,

Montreal, Quebec, Canada. Once methane hydrate was formed in the sediment in the cell, excess methane gas above the sediment was replaced by CO_2 gas. The head pressure was maintained at 550 psia by a high-pressure pump. Small samples were extracted from the gas phase in the cell above the sediment hydrate at constant pressure maintained by the pump. Methane and CO_2 content were analyzed using a Hewlett Packard (HP) gas chromatograph three times: at the start, after 68 hours, and after 92 hours. The data were collected and analyzed. The results of these tests confirm that the methane gas released from the hydrate field was displaced by CO_2.

[0023] As shown in Fig. 2, methane hydrate was formed, based upon the use of a calculated 0.0263 moles of methane, in the sediment at 3.5°C during the cooling run. The system was then cooled to about 2°C and held at that temperature for 2 hours. The laser images in Figs. 3 and 4, generated at the initiation of CO_2 injection into the sapphire cell, show the methane hydrate (seen as "white" specks) embedded in the sediment close to the surface at 2°C. The laser image in Fig. 5, generated after 92 hours of CO_2 injection, shows hydrate formation (also seen as "white" specks) deeper in the sediment. These images clearly show hydrate in the voids of the sediment. However, it is not possible from the images alone to ascertain whether the hydrate shown in Fig. 5 is methane hydrate or CO_2 hydrate. Rather, determination of the hydrate type may be inferred from an analysis of the vapor phase exiting the sapphire cell. In particular, gas chromatographic analysis of the vapor phase confirmed that the gas released at the end of the test (i.e. after 92 hours of CO_2

injection) was 99.6% methane. From this data, it may be inferred that the methane gas in the vapor phase, initially present in the form of methane hydrate, was displaced by CO_2 to form CO_2 hydrate in the sediment

[0024] Fig. 6 shows the gas chromatographic analysis of the sample from the gas phase (a single peak representative of 100 mole % CO_2) at the start of the test. Fig. 7 shows the gas chromatographic analysis of the sample from the gas phase after 68 hours (two peaks, one of which is representative of 27.67 mole % of methane). After the first sampling, thermodynamic material balance calculations indicated that 0.0235 moles (89.35 %) of methane were released out of the total 0.0263 moles of methane utilized in the hydrate sediment. At the end of 92 hours, gas chromatographic analysis of the gas-phase sample confirmed a methane content of 17.97 mol %. After the second sampling, similar calculations indicated that 0.0262 (cumulative) moles (99.6%) of methane were released out of the total 0.0263 moles of methane from the hydrate sediment. The number of moles used to form the hydrate agrees substantially with the number of moles of methane released at the end of the experiment, indicating the recovery of virtually all of the methane gas used to form the methane hydrate.

[0025] Implementation of the method of this invention may be carried out in a variety of manners. One of the simplest implementations involves the use of concentric conduits in which the carbon dioxide is injected through the inner conduit into the methane hydrate field and displaced methane is collected in the annular

region between the inner and outer concentric conduits for transmission away from the resulting carbon dioxide hydrate field.

[0026] While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for the purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of this invention.